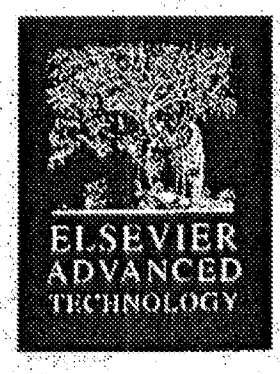
ADDITIVES for PLASTICS Handbook

John Murphy



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Chapter 14: Plasticisers

Short-cut information: **Plasticisers**	
Function	Added to make a compound more flexible, easier to process; mainly used with PVC; also for cellulosics
Properties affected	Flexibility, viscosity
Materials/ characteristics	Monomeric: esters of phthalates, adipates, mellitates Polymerisable esters: di-phthalate ester
Disadvantages	Migration; strict compliance with food contact regulations
New developments	Greater efficiency at lower addition levels, easier mixing; replacement of potentially hazardous types; reduction of leaching/migration

Plasticisers

Many thermoplastics require an additive to 'plasticise' them, either to render the base material processable, or to extend the range of properties, to repeatedly flexible, and flexible at low-temperature (sub-zero and well below). Plasticisers are low molecular or oligomeric additives which are compatible with rigid thermoplastic polymers, rendering them semi-rigid or leathery/rubbery in behaviour. They can be either non-polymeric materials or polymer impact modifiers. Some forms of copolymerisation can also produce a degree of internal plasticising. Certain plasticisers can also perform other functions, assisting in viscosity control, dispersion of particulate additives such as fillers and pigments, and general lubrication of the compound (including mould release).

The largest user by far of plasticisers (about 80%) is PVC, which is unprocessable without a plasticiser, and can be made in either rigid or flexible forms.

The main groups of plasticisers are:

Phthalic acid esters:	
Diethyl hexyl phthalate (usually called dioctyl phthalate - DOP)	Most widely used: good gelling, relatively non-volatile under heat, satisfactory electrical properties and highly elastic compounds with reasonable cold strength
Diisotridecyl phthalate (DITDP)	Long-term heat-resistance up to 105°C
Phthalates of straight-chain C_9H_{19} alcohols	Good non-volatile behaviour and good low-temperature properties
Esters of adipic and sebacic acid:	
Diisodecyl adipate (DIDA)	Less volatile than dioctyl ester (DOA, DOS)
Citric acid esters	Physiologically harmless: used in food industry
Polyglycol fatty acid esters	Good low-temperature resistance (to -30°C) and long-term heat resistance (100°C): addition of 0.05% bisphenol A prevents splitting of oxo-alcohol-ester plasticisers under heat-stress
Tricresyl phosphate (TCP, TCP)	Outstanding heat-resistance, good electrical properties, weather resistance, flameproof: not resistant to low temperatures; should not be used for products in contact with the skin. Other phosphates have lower resistance to heat.

Aromatic sulphonic acid alkyl ester	Midway between DOP and TCP in plasticising properties: widely used in Germany
Oligomeric/polymeric plasticisers	Suitable for pastes (oligomeric) and extrusion/calendering compounds (polymeric): non-migratory, scarcely volatile, low dependency on temperature: some types resist extraction by aliphatic hydrocarbons, mineral oils or fats, some difficult to incorporate/compatible with PVC only in mixes
EVA/CEVA graft polymer	Soft films without plasticiser
Epoxidised soya bean oil, epoxidised esters	Combine functions of plasticising and stabilising

Source: Manufacturers' literature and International Plastics Handbook

Epoxidised grades (soya bean oil, linseed oil) are used as stabilising plasticisers with properties of migration resistance, in PVC compounds, alkyd resins and chlorinated rubbers, and as pigment dispersing agents in plasticised PVC. Alkyl epoxy stearate plasticisers are used as low viscosity stabilisers, especially in PVC pastes, with some grades providing good low temperature properties. They are in liquid form. Soya bean grades have widespread approval for food contact. Advice should be sought for other types.

Esters of fatty acids and monocarboxylic acids can be used as viscosity depressants in PVC pastes and also as secondary plasticisers for plasticised PVC compounds. They are in liquid form. Advice should be sought on food contact approval. Stearic acid esters are used as plasticisers and processing agents for various plastics and also as lubricants for polystyrene. They are semi-solid and have general food contact approval.

Sebacates and adipates are good low temperature plasticisers for PVC, in liquid form, with fairly general food contact approval.

Phthalic acid esters of high molecular weight alcohol are used as special plasticisers for PVC, in liquid or semi-solid form. Diisotridecyl phthalate (liquid) is used for heat-resistant cables and dimethyl cyclohexyl phthalate (liquid) is a special plasticiser for underbody automobile coating.

Trimellitic acid ester (liquid) is a highly heat-resistant plasticiser, pre-stabilised for cable applications.

Polymeric plasticisers in PVC offer good low temperature performance. Monomeric plasticisers are derived from esterification of phthalic anhydride, or trimellitic

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Chapter 15: Process modifiers and processing aids

Short-cut information:

Process modifiers and processing aids

Function	Improvement of processability of compounds: lubrication, higher output/lower energy Modification of polymer properties: nucleation for greater product homogeneity; clarifying agents for improved transparency
Properties affected	Productivity Product quality, transparency
Materials/ characteristics	Fluoropolymers Sorbitol clarifying agents Elastomeric property modifiers, polybutene, acrylic Silicone modifiers MBS, acrylic impact modifiers Fatty acid dispersion aids
Disadvantages	No significant disadvantages known
New developments	Improvement in productivity, energy requirement for processing

Resin modifiers

Thermoplastics

Polybutene as a modifier in polypropylene/ethylene-propylene elastomer blends gives flexible compounds with good impact strength and processability. A recent study (by Amoco) showed that at a level of about 30% of the elastomer content there is no break impact at -20°C, while flexural modulus values are 27,000-38,000 psi and melt flow is 80-100% higher than the unmodified blends (contributing to better processability). Although polybutene reduces the tensile strength, heat distortion temperature and hardness of the blends, compounds have a good balance of properties.

Potential applications include flexible automotive components such as air bag door covers and mud-guards, gasketing and wire jacketing and replacement of plasticised PVC in toys, sporting goods, tools and other consumer items.

Extrusion-grafted (maleated, aminated) polyolefin-based polymers (such as *Exxelor*, from Exxon) are used as impact modifiers, compatibilisers and adhesion promoters, giving a valuable combination of properties for high-value applications:

- Impact modification of engineering thermoplastics
- Compatibilisation of polymer blends, in alloying and recycling
- Adhesion enhancement of polyolefins to metal, glass and polar substrates, by coextrusion, CTR and extrusion coating
- Polymer matrix adhesion to reinforcing agents, such as glass fibre and inorganic fillers, and to flame retardants, such as magnesium hydroxide
- Adhesion of EPDM elastomers to polar substrates, for radiator hoses and V-belts, and of general purpose rubbers to carcass in tyre sidewall compounds is also improved, as is co-vulcanisation of EPDM with polar rubbers

They offer low levels of residual ungrafted monomers, minimising industrial hygiene problems and offer good colour with low level of contaminants and easy handling in compounding operations.

Elastomer modification

What is claimed to be an original technology for modification of nylon 6 with conventional acrylic rubber in granule form has been developed by EniChem Elastomeri. Previously acrylic elastomers were used only in the rubber industry and conventional polymers (EEA or core-shell acrylate polymers) are based on the rubber in hard phases. Europrene AR, however, is based on a soft phase only, which increases the specific

rubber efficiency in the impact resistance characteristics, so differing from other traditional elastomers (EPR, SEBS) used in modification of nylon.

Extensive laboratory tests have shows that super-toughness level is obtained with only 17% Europrene AR and impact resistance characteristics are better than those obtained with 20-25% of other elastomers. Both the low level of rubber and intrinsic characteristics of the soft-phase acrylic increase the resistance to high temperature (Vicat B = 170°C) and the flexural modulus of modified nylon. The high thermal/mechanical inertia and the polarity of these rubbers also allows post-treatments to the nylon which were not previously possible.

New technology to harness silicones

New technology aimed at utilising the properties of silicones more effectively in additives has been announced by Wacker Chemie GmbH. Silicones offer a combination of properties which makes them interesting as modifiers for plastics, improving impact resistance and giving resistance to change in temperature and weathering. But, because they are not compatible with organic polymers, it has often proved difficult to incorporate them into organic polymer systems. In particular, distribution and domain size of the silicone phase has been difficult to control.

Wacker has developed what it describes as 'core-shell particles': flexible silicone cores surrounded by an organopolymer shell, with precisely defined particle sizes and very narrow particle-size distribution. The organic shell makes the particles highly compatible with other organic polymer systems, allowing selective adjustment of the silicone modified phase in the host polymer compound.

Properties which can be conferred by these additives include low temperature flexibility, resistance to changing temperatures and UV resistance. Undesirable effects, such as release and depression of surface tension, which in the past have been caused by migration of the silicone, have not been observed.

Impact modifiers - PVC

Impact modifiers for PVC include methyl butadiene styrene (MBS) and acrylics.

MBS modifiers improve impact strength of PVC compounds without sacrificing the other characteristics. They are used for a variety of rigid and semi-rigid applications and processes, such as blow moulding of bottles, calendering of film and sheet, extrusion of profiles and injection moulding of technical parts. Some types can also be tailored to suit specific requirements.

Acrylic modifiers significantly improve impact characteristics of PVC without any effect of weatherability. The main applications are profiles, pipes and sheets. Acrylic elastomers are used in the reactor (traditionally the German approach), but acrylic additives are gaining in popularity as an efficient alternative.